

# Anthropogenic organic contaminants in the effluent of a combined sewer overflow: impact on Boston Harbor

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Received 7 June 1999; received in revised form 27 December 1999; accepted 21 January 2000

## Abstract

Effluent from a large combined sewer overflow (CSO) in Boston and receiving waters near the CSO outfall were sampled during dry and wet weather conditions. Surficial sediments were also collected from the vicinity of the CSO and at nearby sites. The samples were analyzed for a variety of organic constituents including organic carbon and nitrogen, linear alkylbenzenes (LABs), coprostanol and polychlorinated biphenyls (PCBs). As judged by the presence of waste-specific markers (LABs, coprostanol), the CSO effluent contains sewage under both dry and wet weather conditions. When rainfall occurs, the concentration of suspended solids and all organic constituents in the particulate phase increase, ultimately approaching those characteristic of untreated sewage. The concentrations of LABs and PCBs in the effluent are strongly correlated, indicating that PCBs in the CSO are derived from sewage inputs. During heavy rainfall, the vast majority (>90%) of the hydrophobic organic substances are associated with suspended particulate matter, whereas during dry weather, a significant fraction resides in the operationally defined 'dissolved' phase. Estimates of the mass emission rates of CSO constituents show that >70% of the suspended particles and >90% of the particulate organic carbon, hydrocarbons and trace organics are discharged during wet weather. Particles in the receiving water appear to be strongly influenced by the CSO effluent during wet weather. Concentrations of PCBs in surficial sediments near the CSO are correlated with those of coprostanol and the LABs, indicating that these compounds are derived from similar sources. Based on the observed correlations, approximately 60–80% of the sedimentary PCBs originate from sewage. Comparison of  $\Sigma$ LAB/coprostanol ratios of effluent particles, surficial sediments and sewage sludges suggest that the vast majority of the marker compounds and the PCBs in sediments are not from the CSO, but are derived from one of two sewage treatment plants that discharged sludge into the harbor

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until 1991. The sludge-derived contaminants were probably carried by tidal currents into Dorchester Bay and deposited in shallow, quiescent embayments where sedimentation is favored. These results illustrate the potential importance of long-range transport of waste-derived contaminants in urban harbors and their rapid accumulation in localized depocenters. Published by Elsevier Science Ltd.

**Keywords:** Boston Harbor; Pollutant loadings; Sewage; Sediment pollution; PCBs; Linear alkylbenzenes; Hydrocarbons; Coprostanol

## 1. Introduction

For many years, Boston Harbor served as receiving waters for virtually all of the wastes and by-products generated by metropolitan Boston and 42 surrounding communities. This led to widespread chemical and bacterial contamination of water and sediment environments (e.g. Boehm, Steinhauer & Brown, 1984; Fitzgerald, 1980; Gardner & Pruett, 1987; NOAA, 1988; Rex et al., 1992; Shiaris & Jambard-Sweet, 1986; Shiaris et al., 1987). Studies undertaken in the 1980s and 1990s established that municipal wastes, both treated and untreated, were the largest sources of most pollutants and pathogenic microorganisms to the harbor (MIT Sea Grant, 1998; Shea & Kelly, 1992).

The Massachusetts Water Resources Authority (MWRA) stopped discharge of sewage sludge to the harbor in December 1991. Aggressive source control and better wastewater treatment facilities have led to measurable improvements in the quality of the wastewater effluent (Sung & Higgins, 1998). Recent studies provide evidence that the harbor is recovering (Bothner, Buchholtz ten Brink & Manheim, 1998; Rex, 1993). However, the sediments remain polluted (Leo, Alber, Connor, Keay & Rex, 1993; Long, Sloane, Carr, Scott, Thursby & Wade, 1996), and complete recovery is expected to take many years.

Before 1998, sewage treatment plants on Deer Island and Nut Island (Fig. 1) served the Boston metropolitan area. At the time of the present study (1988–89) these plants discharged approximately 1.8 billion liters of primary treated effluent and 70 dry tons of sludge to the harbor each day. During wet weather, inflows could exceed the capacity of the wastewater treatment systems, and raw sewage and runoff was directed to relief drains known as combined sewer overflows (CSOs). This resulted in the discharge of untreated wastes directly to Boston Harbor. As of 1989, there were 108 such CSOs (MDC, 1984), but little was known of their impact on the harbor environment. Consequently, a multidisciplinary study was undertaken to examine baseline biological and chemical conditions in the vicinity of one of the largest CSOs (at Fox Point; Fig. 1) and to assess effects this system might be having on the harbor.

There were four components of the study. Benthic biological community structure (Gallagher & Grassle, 1989), the incidence of neoplasia in hemolymph of the intertidal clam, *Mya arenaria* (Reinisch, Yanong & Craig, 1989), and chemical studies involving trace metals and  $^{210}\text{Pb}$  sediment chronologies (Wallace, Krahforst, Pitts, Shine, Studer & Bollinger, 1991) are presented elsewhere. This paper describes an investigation of the organic chemistry of the CSO effluent, receiving water and sediments. (The full study and all data are given in a report by Eganhouse & Sherblom,

1991, which can be obtained upon request.) We targeted several classes of trace organic compounds: the linear alkylbenzenes (LABs), coprostanol and the polychlorinated biphenyls (PCBs). The LABs are produced industrially in the synthesis of linear alkylbenzenesulfonates (LAS), the most widely used anionic surfactants in the USA (cf. Takada & Eganhouse, 1998). LABs occur as trace components in detergent formulations and are introduced into municipal waste streams from domestic and industrial detergent use. Consequently, the LABs have been proposed as molecular markers of municipal waste in the environment. Coprostanol (5 $\beta$ -cholestan-3 $\beta$ -ol) is a major sterol in mammalian feces that has often been used as an indicator of human wastes in the environment (cf. references in Takada & Eganhouse, 1998). We were interested in coprostanol as a marker of untreated sewage in the CSO effluent and harbor environment. The PCBs were chosen for study because they have been identified as one the most important classes of contaminants in Boston Harbor (Boehm et al., 1984; NOAA, 1988).

The objectives of the present study were: (1) to characterize the organic chemical composition of CSO effluent and harbor water in the vicinity of the CSO; (2) to estimate mass emission rates of anthropogenic organic contaminants from the CSO to the harbor; and (3) to assess impacts of the CSO on the local environment. To the best of our knowledge, this work is part of the most comprehensive multidisciplinary study of a large CSO releasing wastes into a major urban harbor.

## 2. Materials and methods

### 2.1. Study site

The study site is in Dorchester Bay in the northwestern portion of Boston Harbor (Fig. 1), a shallow, glacially carved, tidally dominated estuary characterized by

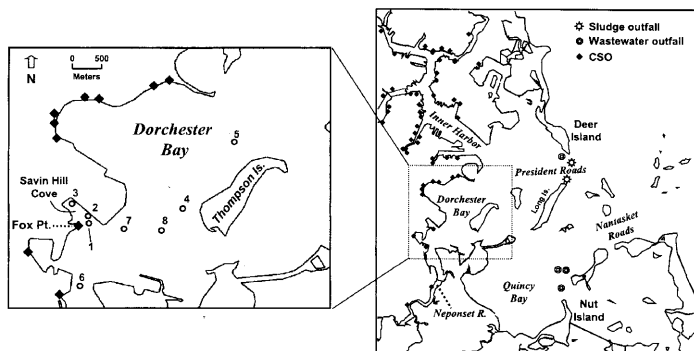


Fig. 1. Map of Boston Harbor with expanded inset of Dorchester Bay showing locations of Fox Point combined sewer overflow (CSO), Savin Hill Cove and sediment sampling stations.

irregular bathymetry and 31 islands. The harbor opens into Massachusetts Bay through two channels: Nantasket Roads and President Roads. At the time of this study, the Deer Island and Nut Island plants released primary treated effluent and sludge from outfalls positioned in or near these channels. The harbor is thought to be flushed by semidiurnal tides in approximately 3–17 days (Signell & Butman, 1992; Stolzenbach, Adams, Ladd, Madsen & Wallace, 1993). However, tidal exchange is much more efficient near the channels than in remote embayments. As much as 80% of the harbor, including the study site, is considered to be depositional. This is a consequence of the weak and variable tidal currents away from the main channels and the protected character of the harbor (Knebel & Circé, 1995; Stolzenbach et al., 1993).

The Fox Point CSO discharges untreated sewage and storm runoff during periods of rainfall. Flow also occurs during dry weather because water enters the CSO by infiltration and because of illegal sewage connections that existed at the time of this study. These wastes, along with harbor water that leaks into the system through the tide gates, are released during ebb tide. Sediments in the subtidal zone immediately adjacent to the CSO are organic-rich silty muds (median grain size = 5 $\phi$ ; Gallagher & Grassle, 1989).

## 2.2. Sampling

### 2.2.1. Water samples

Water samples were collected contemporaneously from the Fox Point CSO and in the harbor proximal to the outfall to evaluate the impact of CSO effluent on the receiving water. To develop estimates of the mass emission rates of suspended solids, particulate organic matter and various trace organic constituents, we determined concentrations of these materials in the CSO effluent under varying flow regimes. Five paired effluent and harbor water samples were, thus, collected for organic chemical analysis (Table 1). Two of the sample pairs (E1/W1, E2/W2) were collected under low flow, dry weather conditions, whereas the other three (E3/W3, E4/W4, E5/W5) were obtained during periods of variable rainfall.

Grab samples of CSO effluent were taken approximately 450 m from the terminus of the outfall within 10 min of peak flow (Wallace et al., 1991). Effluent was sampled with a stainless steel bucket and immediately transferred to amber glass bottles. The bottles were stored on ice until return to the laboratory, whereupon the effluent was filtered as described below. On 11 August 1988, a flow-proportioned composite sample of effluent (E4c) was also collected. Sampling was conducted with a peristaltic pump at 5-min intervals for a period spanning the duration of effluent discharge (ca. 3 h). Surface water was obtained near the CSO outfall using a peristaltic pump.

### 2.2.2. Sediment samples

Surficial sediments were collected at four primary stations (Fig. 1): Savin Hill Cove intertidal (stn. 3), Savin Hill Cove subtidal (stn. 1), Thompson Island subtidal (stn. 5) and Neponset River intertidal (stn. 6). The four primary stations represent highly impacted (Savin Hill Cove) and reference (Thompson Island) environments.

Table 1

Hydrologic information for sampling events and concentration and elemental composition of suspended particulate matter in Fox Point combined sewer overflow (CSO) effluent and harbor water samples, 1988

Sampling date	Sample <sup>a</sup>	Volume discharged <sup>b</sup> (m <sup>3</sup> )	Rainfall <sup>c</sup> (cm)	Effluent				Harbor water			
				TSS (mg/l)	TOC (%)	TN (%)	C/N	TSS (mg/l)	TOC (%)	TN (%)	C/N
3/16/88	E1/W1	1290	0	21.4	7.26	0.85	8.5	29.3	11.8	1.10	10.8
4/1/88	E2/W2	1883	0	20.7	5.95	0.69	8.7	14.1	9.77	1.19	8.2
4/13/88	E3/W3	4352	0.03 <sup>d</sup>	18.3	5.77	0.75	7.7	20.0	6.31	0.83	7.6
7/12/88	E4/W4	5165	1.09	53.4	21.8	3.28	6.6	96.6	13.0	1.64	8.0
7/20/88	E5/W5	4574	1.70	41.0	17.9	2.35	7.6	28.0	8.1	1.08	7.5

<sup>a</sup> En, effluent; Wn, water, where n = 1–5.

<sup>b</sup> Volume of water discharged per sampling event (cf. Wallace et al., 1991, for discussion of discharge calculations).

<sup>c</sup> Rainfall accumulation measured by Montedoro–Whitney RG-1 rain gauge at CSO effluent sampling site (cf. Wallace et al., 1991).

<sup>d</sup> Data collected at Logan Airport.

Additional sediment samples were taken at locations between the Fox Point CSO outfall and the Thompson Island subtidal reference site, stn. 5 (viz. stns. 2, 7, 8 and 4; Fig. 1). Sampling along linearly or exponentially spaced transects was complicated by the presence of a mussel bed and the navigational channel. At most of the subtidal sites, surface sediments (0–2 cm) were collected with a stainless steel Eckman dredge. The only exceptions were samples collected at stations 4 and 5, where short cores were taken by divers using polycarbonate core liners. Sediments from the intertidal sites were collected during low tide using a stainless steel spatula.

### 2.3. Analytical procedures

Details of the procedures and materials used for the analysis of water and sediment samples can be found in Eganhouse and Sherblom (1991). This report is available upon request. Following is an abbreviated description.

#### 2.3.1. Fractionation of water samples

Effluent and harbor water samples to be analyzed for trace organics were filtered using pre-combusted Whatman GF/C glass fiber filters. The particle-bearing filters were stored at –20°C, whereas the filtrates were immediately transferred to separatory funnels for liquid–liquid extraction. Separate aliquots of effluent and harbor water were fractionated on GF/C filters for determination of total suspended solids (TSS) and the total organic carbon (TOC) and total nitrogen (TN) contents of retained particles.

#### 2.3.2. Initial processing of sediment samples

Frozen sediments were thawed and homogenized. An aliquot was taken for determination of water content. This was freeze-dried, reweighed and ground to a

fine powder (for elemental analysis). Separate aliquots of wet sediment (for trace organic analysis) were weighed directly into glass centrifuge bottles.

### 2.3.3. TSS, elemental analysis (particles, sediments)

TSS content in water samples was determined by freeze-drying and reweighing the pre-tared GF/C filters used in filtration. The glass fiber filters containing effluent or harbor water particles were then ground to a fine powder. Inorganic carbon from particulate and sediment samples was removed by exposure to HCl vapors (Hedges & Stern, 1984), and TOC and TN concentrations were determined using a CHN analyzer.

### 2.3.4. Extraction and chromatographic separation procedures

Filtrates, particulate samples and sediments were spiked with recovery surrogates appropriate for the LABs, PCBs and coprostanol (1-phenyl-C<sub>9–14</sub>, PCB congeners 30, 155, 198, and 5 $\alpha$ [H]-androstanol, respectively). Filtrates were extracted with dichloromethane, whereas particulate samples were extracted in a Soxhlet apparatus using a 9:1 mixture of dichloromethane/methanol. Sediments were extracted at ambient temperature on a shaker table using methanol followed by dichloromethane.

All extracts were concentrated by rotary evaporation (< 30°C). An aliquot of the extract was transesterified with BF<sub>3</sub>-methanol and treated with anhydrous Na<sub>2</sub>SO<sub>4</sub> and activated copper to remove residual water and elemental sulfur, respectively. The extract was concentrated to a small volume and analyzed for total extractable organic matter (TEO) content using a microbalance.

Thin-layer chromatography (TLC) was used for separation of total hydrocarbon (THC) and alcohol (ALC) fractions (Eganhouse, 1982), yields of which were determined gravimetrically. PCBs were isolated by column chromatography (cf. Eganhouse, Gould, Olaguer, Sherblom & Phinney, 1987; Eganhouse, Gould, Olaguer, Phinney & Sherblom, 1989).

The THC fraction was evaporated under a stream of nitrogen and taken up in a solution containing 1-phenyl-C<sub>15</sub> (internal standard). Concentrations of 26 LABs (C<sub>10–14</sub> chain lengths) were determined by high resolution gas chromatography/mass spectrometry (HRGC/MS; Eganhouse, Olaguer, Gould & Phinney, 1988). All THC fractions were analyzed by full scan HRGC/MS to identify specific hydrocarbons (see below). Sterols present in the ALC fraction were converted to the corresponding acetates and further purified by TLC. The sterol acetates were taken up in a solution of 5 $\alpha$ [H]-cholestane (internal standard) and analyzed for coprostanol acetate by HRGC/flame ionization detection (Eganhouse et al., 1988). The PCB fraction was taken up in a solution containing PCB congener 169 (internal standard) and analyzed on a Varian 6000 HRGC equipped with a <sup>63</sup>Ni electron capture detector (Eganhouse et al., 1989). This method yields concentrations of as many as 130 PCB congeners in  $\leq$  96 chromatographic peaks. Total PCB concentrations ( $\Sigma$ PCBs) were determined by summing concentrations of individual peaks which had been confirmed as PCBs by HRGC/MS. No standard reference materials were available to evaluate the accuracy of PCB, coprostanol and LAB determinations in water and sediments at the time of this study. However, measurements made on replicate samples showed that precision was, in all cases, within 15%.

### 3. Results and discussion

#### 3.1. CSO effluent/harbor water

##### 3.1.1. Bulk properties (TSS, TOC, TN)

TSS concentrations of the effluent samples range over a factor of three (18–53 mg/l; Table 1). They are much lower than those typically observed for treated municipal wastewater effluents (Mueller & Anderson, 1983) but fall within the range reported for urban stormwaters (Hoffman, Latimer, Mills & Quinn, 1982; Hoffman, Mills, Latimer & Quinn, 1984). TSS concentrations of 20–220 mg/l were determined in a study of the Fox Point CSO effluent during wet weather conditions (Camp, Dresser & McKee, 1981).

TOC concentrations of particles in the CSO effluent range from 6 to 22%, whereas TN content varies between 0.7 and 3.3%. These are within ranges reported for suspended matter in municipal waste effluents (Eganhouse & Kaplan, 1988; Myers, 1974; Sweeney, Kalil & Kaplan, 1980) and urban runoff (Eganhouse, 1982) from southern California. The effluent particles collected in this survey generally exhibit C/N ratios of 7–9. Other data for suspended matter in wastewater effluents (Eganhouse & Kaplan, 1988) and urban stormwater runoff (Eganhouse, 1982) from southern California have generally indicated higher C/N ratios (12–15 and 10–28, respectively) typical of terrestrial organic matter that is depleted in nitrogen. The enrichment of nitrogen in the CSO effluent may indicate the presence of significant amounts of protein-rich particulate material. TSS concentration and organic matter content increased with increasing rainfall (cf. Table 1) and were strongly correlated ( $r^2=0.99$ ). Organic-rich particles may be introduced or resuspended into the CSO effluent during heavy rainfall, probably from inputs of raw sewage.

Harbor water samples collected during peak effluent flow are expected to represent a mixture of ambient harbor water at low tide and recently discharged effluent. The TSS concentrations of the harbor water samples generally fall within 14–30 mg/l, excluding the sample collected on 12 August 1988 (W4). Stolzenbach et al. (1993) indicate that TSS concentrations in the harbor typically range from 1–10 mg/l. In general, the TSS concentrations of the effluent and harbor water samples are quite similar, but there is no obvious correlation between the concentrations of TOC and TN in harbor water particles and effluent particles sampled at the same time. The C/N ratios of harbor water particles are from ca. 7.5 to 11. This is similar to ratios obtained for the effluent particles. With the possible exception of samples collected under high flow, wet weather conditions, it would appear that impacts by the CSO on harbor water are not reflected in the TSS concentration and elemental abundance of the suspended matter.

##### 3.1.2. Extractable organic matter: abundance and composition

TEO concentrations of filterable particulate matter in the effluent range from about 4 to 31 mg/l (or 200–750 mg/g; Table 2). This compares with an 'oil and grease' concentration of 12 mg/l observed in Fox Point CSO effluent during wet weather (Camp, Dresser & McKee, 1981). As in the case of the TSS and particulate

Table 2

Concentration of total extractable organic matter and total hydrocarbons in suspended particles isolated from Fox Point combined sewer overflow (CSO) effluent and harbor water samples<sup>a</sup>

Sample	Concentration (mg/l)		Concentration (mg/g)	
	TEO	THC	TEO	THC
E1	4.4	0.26	200	12
E2	4.1	0.28	200	14
E3	6.4	0.44	230	24
E4	—	5.1	—	96
E4 <sup>c</sup>	23	4.3	430	80
E5	31	6.1	750	150
W1	3.4	1.2	120	42
W2	—	0.77	—	55
W3	—	0.55	—	28
W4	—	4.1	—	42
W5	2.2	0.72	80	26

<sup>a</sup> TEO, total extractable organic matter; THC, total hydrocarbons.

<sup>b</sup> This sample is a flow-proportioned composite. See text for explanation.

organic matter content, TEO concentrations of suspended matter appear to increase with rainfall accumulation.

The highest volume-based concentrations of TEO in the CSO effluent samples are similar to the lowest concentrations reported for treated municipal wastes (Eganhouse & Kaplan, 1982), but they overlap the range found for urban stormwater runoff (Eganhouse & Kaplan, 1981). The solids-based concentrations are similar to or exceed those found in treated municipal wastewaters (Eganhouse, 1986; Eganhouse & Kaplan, 1982), and they greatly exceed those found in Los Angeles River stormwater runoff (Eganhouse & Kaplan, 1981). Extractable organic matter comprises 20–75% of the particulate matter in the CSO effluent. Thus, suspended particles in the effluent are extremely lipid-rich and more closely resemble suspended matter in sewage than in urban runoff.

Under dry weather conditions, volume-based THC concentrations of CSO effluent particles are low (<1 mg/l), similar to those found in urban runoff during dry weather conditions (Eganhouse & Kaplan, 1981). Effluent samples taken from the Fox Point CSO during wet weather, however, exhibit THC concentrations within the range typical of urban stormwater runoff (>1.0 mg/l; Eganhouse & Kaplan, 1981; Hoffman et al., 1982) or treated wastewater effluent (Barrick, 1982; Eganhouse & Kaplan, 1982; Van Vleet & Quinn, 1977). The higher solids-based THC concentrations observed in the CSO effluent fall in the range characteristic of municipal waste effluent or storm runoff (25–75 and 10–70 mg/g, respectively), whereas the lower concentrations are more consistent with data for dry weather runoff (<25 mg/g; Eganhouse & Kaplan, 1981; Hoffman et al., 1982).

The composition of the hydrocarbon fractions isolated from effluent and harbor water particles is illustrated in Fig. 2. The distributions are complex and are



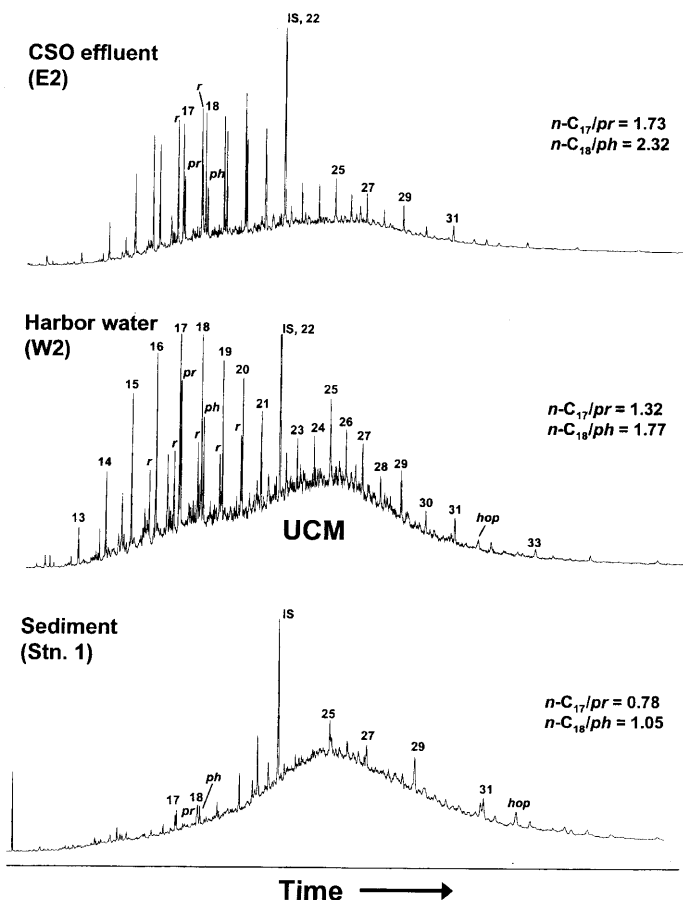


Fig. 2. High resolution gas chromatograms of total hydrocarbon fractions from Fox Point combined sewer overflow (CSO) effluent particles (E2-4/1/88), harbor water particles (W2-4/1/88), and surficial sediments (stn. 1) collected near the CSO outfall. *r*, LAB recovery surrogates; IS = 1-phenyl- $\text{C}_{15}$  (internal standard); pr, pristane; ph, phytane; hop, hopane; UCM, unresolved complex mixture. Numbers above peaks indicate chain length of normal alkanes.

characterized by a unimodal or bimodal unresolved complex mixture (UCM). The UCM is comprised largely of a mixture of aliphatic hydrocarbons (branched and cyclic) which elute in the region  $n\text{-C}_{13}$  to  $> n\text{-C}_{36}$ . UCMs with these characteristics are attributable to the presence of fossil fuels, and, except under restricted circumstances,

are not believed to arise from recent biogenic sources (Volkman, Revill & Murray, 1997). The major resolved components consist of normal, acyclic isoprenoid and polycyclic aliphatic hydrocarbons. The aliphatic hydrocarbons include multiple homologous series of: *n*-alkanes ( $C_{13-36}$  with little or no odd-even predominance), alkylcyclohexanes, head-to-tail acyclic isoprenoids, regular ( $C_{27-29}$ ) steranes, and pentacyclic triterpanes ( $C_{27,29-35}$ ;  $C_{30}$  dominant) having  $17\alpha(H),21\beta(H)$ -stereochemistry. The extended hopanes ( $C_{31-35}$ ) occur as diastereomeric pairs (22S and 22R) in abundance ratios of 3:2. The dominance of the UCM suggests that much of these hydrocarbons comes from weathering of fossil fuels and/or residues of crankcase oil (Eganhouse, Simoneit & Kaplan, 1981; Hoffman et al., 1984; Volkman et al., 1997).

Hydrocarbon compositions of harbor water particles were similar to effluent samples taken at the same time. However, a consistent difference is that the harbor water samples, especially those collected during dry weather, low flow conditions, had larger UCMs than the corresponding effluent samples (Fig. 2). In addition, the ratios, *n*- $C_{17}$ /pristane and *n*- $C_{18}$ /phytane, were higher in effluent samples than in the corresponding harbor water samples. These trends suggest that the hydrocarbons associated with particulate matter in the harbor water samples are probably a mixture of CSO effluent and a second source of weathered and/or biodegraded petroleum. As shown in Fig. 2 (lower panel), resuspended sediments are the most likely candidates for this second source. During high flow, the hydrocarbon compositions of paired effluent and harbor water samples are more nearly identical, reflecting the greater influence of CSO effluent particles.

### 3.1.3. Trace organics

We encountered difficulties with the determination of coprostanol in some water samples such that reliable data for only one sample pair (E4/W4) was obtained. Therefore, the following discussion focuses largely on results for the LABs and PCBs. As shown in Table 3, effluent particle  $\Sigma$ LAB concentrations range from 0.09 to 2.3  $\mu\text{g/l}$ , 4 to 55  $\mu\text{g/g}$  and 60 to 310  $\mu\text{g/g}$  OC. Under dry weather or light rain conditions (E1–E3) approximately 40–60% of the LABs are found in the particulate phase. Given the hydrophobicity of these compounds ( $\log K_{ow}=6.9-9.95$ ; Sherblom, Gschwend & Eganhouse, 1992), this distribution may indicate the presence of significant amounts of colloids capable of passing glass fiber filters (Takada, Ogura & Ishiwatari, 1992). During moderate to heavy rainfall (E4, E5) particulate  $\Sigma$ LAB concentrations rise dramatically, and the vast majority of the LABs (80–92%) are associated with filterable particulate matter. The particulate  $\Sigma$ LAB concentrations (volume basis) range over a factor of more than 20, but the range is reduced by normalization to dry mass (factor of 12) or organic carbon content (factor of 5). This clearly identifies particulate matter, especially organic-rich particles, as the carriers of these compounds. The higher volume-based effluent concentrations are similar to the lower concentrations reported for suspended particles in untreated wastewater influent (1.0–5.6  $\mu\text{g/l}$ ; Takada & Ishiwatari, 1987), and concentrations on a dry solids basis fall within the range reported for these same wastes (6–60  $\mu\text{g/g}$ ). Primary treatment of sewage results in removal of LABs largely by sedimentation of

Table 3

Summary of results for trace organic analyses of particulate matter in Fox Point combined sewer overflow (CSO) effluent and harbor water samples

Sample	Linear alkylbenzenes (ΣLABs) <sup>a</sup>			I/E ratio <sup>d</sup>	Polychlorinated biphenyls (ΣPCBs) <sup>b</sup>		
	μg/l <sup>c</sup>	μg/g	μg/g OC		μg/l <sup>c</sup>	μg/g	μg/g OC
<i>Effluent</i>							
E1	0.09 (43)	4.4	60	0.86	0.019 (50)	0.90	12
E2	0.22 (64)	11	18	0.99	0.022 (92)	1.0	18
E3	0.16 (61)	8.7	150	0.83	0.026 (79)	1.4	25
E4	0.85 (80)	16	73	0.88	0.51 (94)	9.5	42
E4 <sup>e</sup>	1.2 (83)	22	100	1.0	0.34 (98)	6.4	29
E5	2.3 (92)	55	310	0.61	0.73 (99)	18	100
<i>Harbor water</i>							
W1	0.36 (81)	12	100	0.88	0.11 (88)	3.6	31
W2	0.36 (99)	26	260	0.86	0.037 (56)	2.6	27
W3	0.24 (80)	12	190	0.89	0.031 (79)	1.5	24
W4	0.74 (98)	7.6	59	1.0	0.015 (28)	0.16	1.2
W5	0.34 (84)	12	150	0.75	0.044 (76)	1.6	19

<sup>a</sup> Total LAB concentration ( $\Sigma$ LABs) is the summation of  $C_{10-14}$  linear alkylbenzenes.

<sup>b</sup> Total PCB concentration ( $\Sigma$ PCBs) is the summation of all individual congeners (cf. Eganhouse et al., 1989).

<sup>c</sup> Number in parentheses is the percent of  $\Sigma$ LABs or  $\Sigma$ PCBs in the particulate phase.

<sup>d</sup> See text for definition of I/E ratio.

solids rather than biodegradation (Takada & Ishiwatari, 1987). Thus, particles present in the CSO effluent under heavy rainfall conditions would appear to be equivalent to those in slightly diluted raw sewage. The presence of LABs in samples E1–E3 demonstrates that even under dry weather conditions, the CSO effluent contains measurable amounts of sewage.

Fig. 3 presents data for  $\Sigma$ LAB concentrations (particulate phase) in CSO effluent and harbor water samples along with data for sludge samples collected from the Deer Island and Nut Island treatment plants (Eganhouse et al., 1988). In addition, an index of the extent of LAB biodegradation, the I/E ratio, is provided. This ratio, given as:

$$\text{I/E ratio} = \frac{[6\text{-phenyl-}C_{12} + 5\text{-phenyl-}C_{12}]}{[4\text{-phenyl-}C_{12} + 3\text{-phenyl-}C_{12} + 2\text{-phenyl-}C_{12}]},$$

reflects the relative abundance of 'internal' isomers (e.g. 6-phenyl- $C_{12}$ ) and 'external' isomers (e.g. 2-phenyl- $C_{12}$ ). Laboratory and field studies have shown that the external isomers are degraded more rapidly than the internal isomers (Bayona, Albaigés, Solanas & Grifoll, 1986; Eganhouse, Blumfield & Kaplan, 1983; Takada & Ishiwatari, 1987, 1990). Hence, the I/E ratio tends to increase as biodegradation proceeds. In a detergent or primary treated wastewater, the I/E ratio typically is less than or near 1, whereas ratios measured in laboratory incubation experiments and in environmental samples fall in the range of 2–6 (cf. Takada & Eganhouse, 1998).

When normalized to TEO and especially dry mass,  $\Sigma$ LAB concentrations in effluent tend to increase with rainfall accumulation (Fig. 3). During wet weather (E4, E5) concentrations on a dry mass basis approach those in Deer Island (but not Nut Island) sludge. At the time of this study, Nut Island sludge had a  $\Sigma$ LAB content approximately 10 times higher than Deer Island sludge because an industrial LAB sulfonating facility was discharging wastes to the Nut Island plant (M. Ross, MWRA, personal communication). Moreover, the Deer Island treatment plant serviced a large part of Metropolitan Boston, integrating influents from the same municipalities as did the Fox Point CSO during overflow conditions. It is, therefore, not surprising that the  $\Sigma$ LAB concentrations of Deer Island sludge are essentially equivalent to those found in the CSO effluent particles under moderate to heavy rainfall conditions. This further supports the conclusion that when heavy rainfall events occur, a large fraction of the particles in the effluent are derived from untreated sewage. Because the I/E ratios for all effluent samples and sludges are below or near unity (0.61–1.0; Table 3) it would appear that little or no biodegradation of the LABs had occurred at the time these wastes were discharged. Moreover, the presence of the LABs with low I/E ratios in the CSO effluent during dry weather (E1–E3) must be primarily due to chronic leakage and infiltration of domestic wastes rather than inputs of degraded deposits in the pipe or from the harbor. I/E ratios for harbor water samples were also near unity (0.74–1.0; Table 3), whereas the ratio for surficial sediments near the outfall (stn. 1) was 2.4. These findings are consistent with the hypothesis that CSO effluent particles, rather than resuspended sediments, dominate harbor waters near the outfall during wet weather.

It is relevant, at this point, to introduce the measurements of coprostanol made on E4 and W4 samples. The concentrations of coprostanol in these samples were 4.97

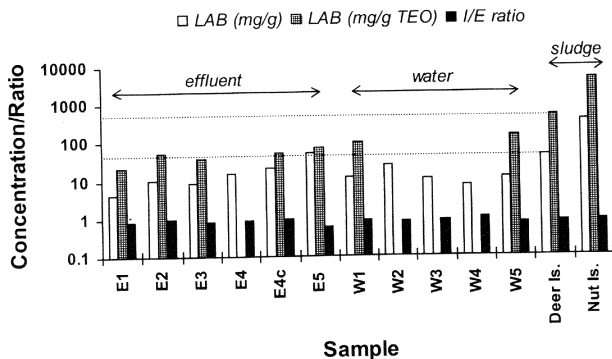


Fig. 3. Concentrations and I/E ratios of linear alkylbenzenes (LABs) in Fox Point combined sewer overflow (CSO) effluent particles (E1–E5), harbor water particles (W1–W5) and sludge samples collected from Deer Island and Nut Island treatment plants (Eganhouse et al., 1988). See text for explanation of I/E ratio. TEO, total extractable organic matter.

and 1.72 mg/g, respectively. These bracket concentrations determined for Deer Island and Nut Island sludges (2.23 and 1.80 mg/g, respectively; Eganhouse et al., 1988). The E4/W4 coprostanol concentration ratio is 2.89, whereas the ratio of  $\Sigma$ LAB concentrations is 2.08. These are reasonably similar and may indicate dilution of CSO effluent particles by particles derived from the harbor in the vicinity of the outfall during high flow conditions. The degree of dilution is relatively low (i.e. 2–3) and is in agreement with estimates made by Wallace et al. (1991) who reported a dilution of ca. 2:1 for the E4/W4 sample pair based on salinity.

If one computes the  $\Sigma$ LAB/coprostanol ratios for these samples, values of 0.003 and 0.004 are obtained (E4 and W4, respectively). The similarity of the ratios for the CSO effluent and corresponding harbor water sample indicates that dilution does not affect marker compound composition. This is consistent with observations made earlier regarding the similarity of hydrocarbon compositions of effluent and receiving water particles during heavy rainfall conditions. The ratios can also be compared with those determined for the Deer Island and Nut Island sludges by Eganhouse et al. (1988) which were 0.021 and 0.210, respectively. Again, the CSO effluent composition more closely resembles Deer Island sludge than Nut Island sludge.

Table 3 also summarizes results of the PCB measurements on particles in effluent and harbor water samples. Effluent concentrations of  $\Sigma$ PCBs range from 0.02 to 0.73  $\mu\text{g/l}$ , 0.9 to 18  $\mu\text{g/g}$  and 12 to 100  $\mu\text{g/g}$  OC. During dry weather/light rain conditions (E1–E3), the particulate PCBs represent 50–92% of the total, whereas during wet weather (E4, E5) they comprise 98–99% of the total.  $\Sigma$ PCB concentrations appear to correlate with rainfall accumulation (cf. Tables 1 and 3), nearly constant levels being observed under dry weather and light rain conditions (E1–E3). There is an increase in effluent (particulate)  $\Sigma$ PCB concentrations of more than one order of magnitude during moderate to heavy rainfall (E4, E5). Metcalf and Eddy (1984) reported data collected by the United States Environmental Protection Agency (US EPA) for the concentration of total PCBs in final effluent of Deer and Nut Island treatment plants during wet and dry weather for the period 1982–1984. Nut Island effluent had concentrations ranging from 0.4 to 2.1 and 0.3 to 8.7  $\mu\text{g/l}$  during wet and dry weather flows, respectively. Deer Island effluent had concentrations ranging from 0.7 to 1.3 and 0.5 to 2.1  $\mu\text{g/l}$  during wet and dry weather flows, respectively. Notwithstanding differences in the methodologies being used (Shea & Kelly, 1992), the EPA data compare well with results for the Fox Point CSO effluent.

The concentrations of  $\Sigma$ PCB in harbor water particles range from 0.02 to 0.11  $\mu\text{g/l}$ , 0.2 to 3.6  $\mu\text{g/g}$  and 1.2 to 31  $\mu\text{g/g}$  OC. Wade, Boehm, Altshul and Brown (1987) indicate that  $\Sigma$ PCB concentrations in Massachusetts Bay water column particles are generally less than 0.0005  $\mu\text{g/l}$ . This is approximately two orders of magnitude lower than the concentrations we observed for four of the five CSO receiving water samples examined here. This highlights the extent of contamination of these harbor waters.

Fig. 4 shows chlorination level plots for paired water samples taken under low and high flow conditions (E2/W2 and E5/W5, respectively), the sediment sample near the outfall (stn. 1) and distributions for three Aroclor mixtures. In general, the PCB compositions in effluent and harbor water particles are similar. They exhibit patterns

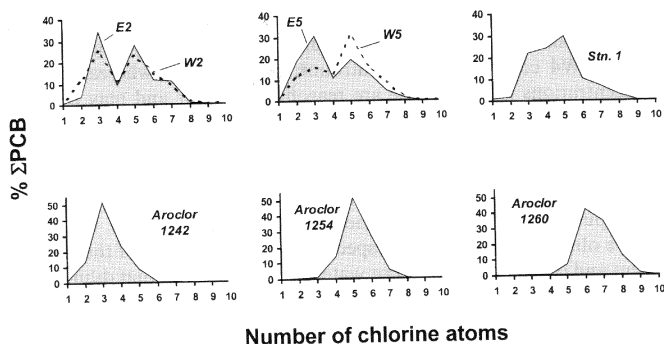


Fig. 4. Polychlorinated biphenyl (PCB) chlorination level plots for: upper panel — particles in Fox Point combined sewer overflow (CSO) effluent/harbor water sample pairs (E2/W2, E5/W5) and surficial sediments collected near the CSO outfall (stn. 1); lower panel — Aroclors 1242, 1254, 1260 (after Eganhouse et al., 1989).

dominated by  $\text{Cl}_3$ - and  $\text{Cl}_5$ -biphenyls. The main difference is the occasional reduced abundance of the  $\text{Cl}_3$ -biphenyls in the harbor water samples. Given the dominance of  $\text{Cl}_5$ -biphenyls in sediments from station 1, the diminution of the  $\text{Cl}_3$  isomer group in harbor water particles may signal dilution of the CSO effluent by PCBs derived from the harbor. Comparison of the isomer group distributions in CSO effluent and harbor water samples with that of the major Aroclors indicates that effluent particles contain PCB assemblages resembling a mixture of Aroclors 1242 and 1254 with possibly lesser amounts of Aroclor 1260. These patterns are similar to those reported by Boehm et al. (1984) for surface sediments taken in the vicinity of Deer Island. In most of the samples they examined within Boston Harbor, the  $\text{Cl}_5$ -biphenyls were dominant with only an occasional indication of a second mode at the  $\text{Cl}_3$  isomer group. Similarly, Gardner and Pruett (1987) reported data for PCB concentrations in sediments of Quincy Bay. All PCB distributions were dominated by Aroclor 1254; Aroclor 1242 was present at concentrations less than one-sixth that of Aroclor 1254. On the basis of  $\Sigma\text{PCB}/\text{coprostanol}$  concentration ratios, Boehm et al. (1984) hypothesized that PCBs in harbor sediments derive mainly from the discharge of municipal wastes. It is interesting, therefore, to observe the strong correlation between  $\Sigma\text{PCB}$  and  $\Sigma\text{LAB}$  concentrations in the CSO effluent samples ( $r^2 = 0.87$ ). This correlation suggests that PCBs associated with suspended matter in the effluent come from the same source as the LABs, namely, sewage.

### 3.2. CSO mass emission rates and mass balance

Estimates of the annual mass emission rates (kg/year) of suspended solids, organic carbon, total hydrocarbons and  $\Sigma\text{PCBs}$  from the Fox Point CSO as of 1989 are presented in Table 4. A detailed description of the procedures used to develop the discharge estimates and their sources of error are given in Wallace et al. (1991).

Table 4

Annual mass emission rates for chemical constituents in effluent of the Fox Point combined sewer overflow (CSO) 1988

Constituent <sup>a</sup>	Mass emission rate (kg/year)	%Discharged during wet weather
Suspended solids	$6.60 \times 10^4$	72
Particulate organic carbon	$1.08 \times 10^4$	90
Particulate nitrogen	$1.51 \times 10^3$	91
THC <sub>part</sub>	$5.98 \times 10^3$	95
THC <sub>part + diss</sub>	$6.37 \times 10^3$	93
ΣPCBs <sub>part</sub>	0.65	97
ΣPCBs <sub>part + diss</sub>	0.67	96

<sup>a</sup> THC, total hydrocarbons; ΣPCBs, total polychlorinated biphenyls; part, constituent associated with particles isolated by filtration; part+diss, constituent associated with particles isolated by filtration + constituent in 'dissolved' phase (i.e. in filtrate).

During wet weather the vast majority of the hydrophobic organic substances (>80–98%) are associated with filterable particulate matter, whereas a significant fraction (as much as 60%) is found in the dissolved (and/or colloidal) phase during dry weather (Table 3). The data indicate that although the discharge of water from the Fox Point CSO during dry weather was of comparable magnitude to that during wet weather, the release of particulate matter took place mainly during storm events (>70%). Consequently, more than approximately 90% of the particulate organic carbon and nitrogen, hydrocarbons and PCBs are discharged from the CSO during wet weather.

One can use these estimates to evaluate the impact of the CSO discharge on the receiving environment by considering a mass balance approach. Using <sup>210</sup>Pb geochronology, Wallace et al. (1991) determined that sediments within the Savin Hill Cove subtidal area were accumulating at a rate of approximately 6.2 cm/year. This rate was applied to an estimated area of the subtidal zone (75,750 m<sup>2</sup>) and measured surficial sediment concentrations to develop estimates of the accumulating masses of sediment, organic carbon and metals in the basin. The results showed that even if all of the particles discharged from the CSO were deposited and remained in the receiving basin, they would make up only a small percentage (<4%) of the total accumulated sediments. In the case of TOC, the CSO discharge could account for approximately 8–10% of the deposited sedimentary organic carbon. Thus, the vast majority of the sediments and organic matter present in Savin Hill Cove appears to be derived from sources other than the Fox Point CSO. As will be shown, molecular markers (i.e. LABs, coprostanol) provide supporting evidence for this conclusion.

### 3.3. Sediments: sources and transport processes

Table 5 summarizes data on the elemental abundance and extractable compound class composition of the sediment samples. Concentrations of TOC for surface sediments range from 1.3 to 4.8%, whereas nitrogen content varies between 0.12 and

Table 5  
Elemental abundance and extractable organics in sediments<sup>a</sup>

Station	TOC (%)	TN (%)	C/N	Concentration of extractables (mg/g)		THC/OC <sup>b</sup>
				TEO	THC	
1	4.5	0.50	9.1	5.6	2.4	530
2	4.8	0.53	9.0	3.9	1.7	360
3	3.8	0.40	9.4	4.7	2.4	630
4	3.6	0.37	9.9	3.2	1.6	430
5	4.0	0.32	12.0	3.0	1.3	320
6	1.3	0.12	11.0	1.4	0.59	460
7	1.9	0.13	14.0	1.6	0.68	360
8	3.6	0.40	9.0	1.6	0.61	170

<sup>a</sup> TOC, total organic carbon; TN, total nitrogen; TEO, total extractable organic matter; THC, total hydrocarbons; OC, organic carbon.

<sup>b</sup> Units of g THC/g OC  $\times 10^4$ .

0.53%, yielding C/N ratios of 9.0 to 14.5. Although the sampling locations selected in this study do not correspond to those of other harbor investigations (Boehm et al., 1984; Bothner et al., 1998; Fitzgerald, 1980; Long et al., 1996; Shiaris et al., 1987), the TOC concentrations and C/N ratios reported here fall within the same ranges (ca. 1–4 and 9–13%, respectively). Durell, Ginsburg and Shea (1991) and Durell (1995) found TOC concentrations of  $3.82 \pm 0.25$  and  $2.54 \pm 1.45\%$  in surficial sediments (0–2 cm) collected near station 1 in November 1990 and August 1994, respectively.

TEO concentrations are 1.6–5.6 mg/g, whereas THC concentrations are 0.6–2.4 mg/g. The higher THC concentrations are comparable to those reported for other municipal waste-contaminated coastal sites (Eganhouse, 1986; Eganhouse & Kaplan, 1988). In all cases, the hydrocarbons dominate the extractable matter (38–51% of TEO) indicating that the more labile, functionalized constituents of the lipids have been lost, and only the most resistant hydrocarbons remain.

The lower panel of Fig. 2 is a high-resolution gas chromatogram of the THC fraction isolated from the Savin Hill Cove subtidal station nearest the outfall (stn. 1). In general, the sedimentary hydrocarbons are characterized by large UCMs extending over a broad carbon chain length range ( $n\text{-C}_{12-36}$ ). In comparison with CSO effluent and harbor water particles, the sediments have lower resolved/unresolved area ratios (i.e. larger UCMs) and lower  $n$ -alkane/isoprenoid ratios indicating that the hydrocarbons have undergone weathering. Such patterns are typical of polluted coastal sediments (Eganhouse & Kaplan, 1988; Van Vleet & Quinn, 1977; Venkatesan, Brenner, Ruth, Bonilla & Kaplan, 1980).

### 3.3.1. Trace organics

Table 6 summarizes results of the LAB, coprostanol and PCB determinations in surficial sediments from Boston Harbor. Also included are data for sediments from other studies in Boston Harbor and Salem Harbor, MA. The concentrations of ELABs in the sediments we examined range from 0.3 to 2.3  $\mu\text{g/g}$ , 8 to 52  $\mu\text{g/g}$  OC



Table 6  
Summary of results for trace organics analysis of sediments from Boston Harbor and other locations

Station/location	Linear alkylbenzenes (ΣLABs)		I/E ratio <sup>a</sup>		Coprostanol <sup>b</sup>		PCBs (ΣPCBs) <sup>c</sup>		Source
	μg/g	μg/g OC	μg/g THC		μg/g	μg/g OC	μg/g	μg/g OC	
1	2.3	52	970	2.4	12	260	0.61	13	This study
2	1.8	38	1100	2.4	8.9	180	0.64	13	This study
3	1.2	33	520	2.8	6.2	160	0.81	21	This study
4	1.6	43	990	2.1	<sup>d</sup>	<sup>d</sup>	0.11	3.1	This study
5	2.0	50	1600	2.4	7.6	190	0.53	13	This study
6	0.49	38	830	2.0	0.89	69	0.20	16	This study
7	0.28	15	410	2.7	0.72	38	0.12	6.3	This study
8	0.29	8.1	480	2.3	0.26	7.3	0.10	2.8	This study
<i>Other studies</i>									
Boston Harbor	<sup>e</sup>	—	—	—	0.6–15.9	162–574	0.014–0.33	3.8–7.8	Boehm et al., 1984
Boston Harbor	—	—	—	—	—	—	0.04–0.83	3.1–18.9	Long et al., 1996
Boston Harbor	0.03–3.20	16.1–91.9	—	—	1.61–32.2	139–1400	0.01–0.35	0.72–13.0	Durell, 1995
Boston Harbor	—	—	—	—	1.0–26.6	—	0.13–1.22	—	Gardner and Pruett, 1987
Boston Harbor	1.2–3.2	22.0–75.0	—	—	4.2–31.0	65–724	—	—	Durell et al., 1991
Salem Harbor	0.04–2.68	3.2–27.1	285–610	0.52–0.72	0.4–14.7	34–202	—	—	Eganhouse, 1986

<sup>a</sup> See text for definition of I/E ratio.

<sup>b</sup> Coprostanol concentrations reported in 'other studies' besides Eganhouse (1986) may include epicoprostanol.

<sup>c</sup> ΣPCB concentrations reported for 'other studies' were determined by various analytical methods that may not be directly comparable.

<sup>d</sup> Alcohol fraction lost.

<sup>e</sup> Dash indicates that no data were available — 'other studies' only.

and 410 to 1600  $\mu\text{g/g}$  THC. These are of the same magnitude as concentrations reported by others for Boston Harbor sediments (Durell, 1995; Durell et al., 1991). Computation of organic carbon-normalized  $\Sigma\text{LAB}$  concentrations reveals that all of the stations in the study area are heavily impacted by waste-derived organic matter with the possible exception of stations 7 and 8.

Concentrations of coprostanol in sediments from this study area are 0.3–12<sup>109/9</sup> or 7–255  $\mu\text{g/g}$  OC. These overlap with ranges reported by Boehm et al. (1984), Durell (1995), Durell et al. (1991), and Gardner and Pruell (1987). Sediments from stations 6, 7 and 8 appear to be considerably less contaminated by sewage based on abundances of this fecal marker.

Finally, Table 6 summarizes results of the PCB determinations. Concentrations of  $\Sigma\text{PCB}$  in the harbor sediments analyzed in this study range from 0.10 to 0.81  $\mu\text{g/g}$ . These compare favorably with measurements made by Boehm et al. (1984), Durell (1995), Gardner and Pruell (1987), and Long et al. (1996) on sediments from other areas of Boston Harbor. However, it is important to recognize that the analytical methods used in these studies differ significantly from ours.

Fig. 5 presents scatterplots of  $\Sigma\text{PCB}$  versus coprostanol,  $\Sigma\text{PCB}$  versus  $\Sigma\text{LAB}$  and  $\Sigma\text{LAB}$  versus coprostanol concentrations in sediments. Although the data are limited, there appears to be a relationship between concentrations of  $\Sigma\text{PCB}$  and coprostanol in the sediments examined in this study ( $r^2=0.71$ ; Fig. 5a) suggesting that much of the PCBs may be derived from sewage. The one exception to this trend is the data point for station 3, which appears to have unusually high concentrations of PCBs. This may reflect a local influence of the Savin Hill storm drain located at the head of Savin Hill Cove. Also shown for comparison (Fig. 5b) are scatterplots of data from Boehm et al. (1984), Durell (1995) and Gardner and Pruell (1987). When these data sets are examined independently or in pooled fashion, no obvious relationship between the measured parameters is found ( $r^2=0.001$ – $0.249$ ). This suggests that either the apparent relationship between  $\Sigma\text{PCB}$  and coprostanol we observed is spurious, or that the relationship only applies within the study area. Although the  $\Sigma\text{PCB}$  versus  $\Sigma\text{LAB}$  correlation shown in Fig. 5c is not as strong as the  $\Sigma\text{PCB}$  versus coprostanol correlation (Fig. 5a), there does appear to be a relationship between these parameters. Assuming the least squares lines shown in Fig. 5a and c accurately represent the relationships between the measured parameters, the similarity of the  $y$ -intercepts suggests that the background, non-sewage  $\Sigma\text{PCB}$  concentration in these sediments is around 0.1–0.2  $\mu\text{g/g}$ . This means that most (i.e. 60–80%) of the PCBs found in heavily contaminated sediments near the Fox Point CSO are derived from sewage.

Fig. 5d presents a scatterplot of  $\Sigma\text{LAB}$  versus coprostanol concentrations in surficial sediments collected in this study. The correlation coefficient obtained by linear regression is high ( $r^2=0.96$ ) indicating that these markers are derived from the same source(s), and the slope is 0.19. As noted earlier, the  $\Sigma\text{LAB}$ /coprostanol ratio for CSO effluent particles was found to be 0.003, whereas ratios for Deer Island and Nut Island sludges were 0.021 and 0.210, respectively (Eganhouse et al., 1988). The slope of the  $\Sigma\text{LAB}$  versus coprostanol line for the sediments is almost identical to the ratio observed for the Nut Island sludge sample and is approximately an order

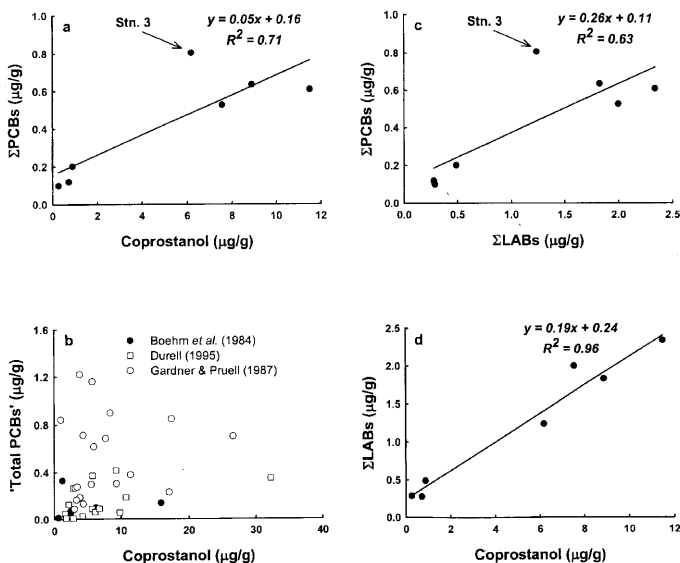


Fig. 5. Scatter plots of: (a) concentration of  $\Sigma$ PCBs versus coprostanol in sediments from the study site; (b) concentration of 'total PCBs' versus coprostanol in sediments from other studies conducted in Boston Harbor (Boehm et al., 1984; Durell, 1995; Gardner & Pruett, 1987); (c) concentration of  $\Sigma$ PCBs versus  $\Sigma$ LABs in sediments from the study site; and (d) concentration of  $\Sigma$ LABs versus coprostanol in sediments from the study site. PCBs, polychlorinated biphenyls; LABs, linear alkylbenzenes.

of magnitude higher than that observed in the CSO effluent particles in sample E4. The discrepancy between marker compound ratios of CSO effluent particles and nearby sediments of nearly two orders of magnitude can be explained by one of two hypotheses: (1) the  $\Sigma$ LAB/coprostanol ratio of the CSO effluent particles is altered during sedimentation; or (2) the  $\Sigma$ LAB/coprostanol ratio is not altered, but inputs of LAB-rich particles are being introduced to the Fox Point subtidal zone from sources outside of the area.

The first hypothesis has not been rigorously tested in either the laboratory or the field. However, one mechanism for alteration of the ratio is that once exposed to the environment, coprostanol associated with effluent particles might degrade more rapidly than the LABs. According to this scenario, the similarity of sediment and Nut Island sludge ratios would be purely coincidental. This mechanism seems unlikely given the number of stations involved and their spatial separation, but definitive experiments on the relative degradation rates of coprostanol and the LABs have not been performed. Thus, it is impossible to evaluate the plausibility of this mechanism. An alternative mechanism is the in situ generation of LABs from LAS

following discharge of CSO effluent particles. To the best of our knowledge, there is no evidence in the literature for such a transformation.

As for the second hypothesis, we have only limited data produced in our laboratory that bear directly on this issue, and they come from Salem Harbor and the Palos Verdes Shelf, CA. The major source of contaminants to sediments at these two coastal locations is believed to be municipal wastes (Eganhouse, 1986; Eganhouse & Kaplan, 1988). Mean  $\Sigma$ LAB/coprostanol ratios of effluent and sediment samples collected near the respective wastewater outfall systems are within a factor of two of each other, and the 95% confidence intervals overlap. The correspondence between effluent and sediment compositions at these sites suggests that the  $\Sigma$ LAB/coprostanol ratio of sewage particles may be conserved. If so, one is left with the inescapable conclusion that the vast majority of the sewage markers, and presumably the PCBs, found in sediments near the Fox Point CSO are derived from sources other than the CSO. Our data suggest that a major source of these contaminants was the Nut Island treatment plant.

It remains to explain how sludge particles discharged from the Nut Island treatment plant could be transported into Dorchester Bay and, ultimately, Savin Hill Cove. At the time of this study, sludge from the Nut Island plant was generally discharged on the outgoing tide. The outfall terminus is at the southern margin of President Roads, north of Long Island (Fig. 1). Even if the sludge was consistently discharged on the outgoing tide, it is unlikely that all of it would be dispersed into waters of Massachusetts Bay. Signell and Butman (1992) have shown that within one tidal cycle only about 17% of the water in Boston Harbor is exchanged for Massachusetts Bay water. Indeed, field observations near the outfall suggest that effluent from the Nut Island sludge outfall remains near Long Island despite strong currents in President Roads (Rex et al., 1992). Signell and Butman (1992) also modeled dispersion of particles released from a point source in Nantasket Roads. They found that the trajectories and distributions of the particles depended strongly on the timing and position of release. The same would probably be true for sludge released at President Roads.

The incoming tide produces relatively large tidal currents over the Nut Island sludge discharge location in the southern section of President Roads. These tidal currents are spatially variable but can reach 80 cm/s (Signell & Butman, 1992) and would be associated with a high boundary shear stress. This would tend to resuspend Nut Island sludge, leading to transport of sludge particles by the tidal currents. Because of the proximity of the Deer Island sludge discharge (on the northern margin of President Roads; Fig. 1), mixing of the two sources of sludge could conceivably occur. Such mixing would result in transport of particles having intermediate  $\Sigma$ LAB/coprostanol ratios into the harbor. However, tidal current charts (Camp, Dresser & McKee, 1981; Knebel, Rendigs & Bothner, 1991) show that much of the transport from the northern margin of President Roads enters the Inner Harbor, not Dorchester Bay, whereas tidal currents on the southern margin of Presidents Roads tend to carry material into Dorchester Bay. Based on model calculations by Lee (1990), Stolzenbach et al. (1993) estimate that as much as 55% of the solids discharged from the sludge outfalls may have been retained in the harbor. From the forgoing discussion, it seems clear that a significant fraction of the Nut Island sludge

could have been transported into Dorchester Bay where it would be available for dispersal and sedimentation in quiescent embayments such as Savin Hill Cove.

#### 4. Conclusions

Combined sewer overflows are used in more than 900 cities in the USA (US EPA, 1998). Many of these municipalities adjoin or are tributary to the coastal zone. Consequently, CSOs represent a potentially significant source of contaminants to urban estuaries. This study has demonstrated that one of the largest CSOs in Boston discharges sewage under both dry and wet weather conditions. Most of the hydrophobic organic contaminants are released during wet weather in association with suspended particulate matter. The impacts of the CSO on the local receiving waters are evidenced by similarities between the organic chemical composition of the effluent particles and those in the receiving waters. These effects are most noticeable during wet weather, presumably due to the greater flows that occur when it is raining. Sediments near the CSO are also heavily impacted by sewage, but the vast majority of the organic matter appears to be derived from outside sources, not the CSO. Based on molecular marker data, we believe the most likely source was the Nut Island sludge outfall located on the southern margin of President Roads. Transport of sludge particles from the outfall into Dorchester Bay (as opposed to Massachusetts Bay) probably occurs because of variable timing of sludge release vis à vis the tides and inefficient exchange at the point of release. The proposed transport pathway, is consistent with known current patterns in the harbor.

The dominance of non-local sources of particles and associated contaminants in sediments near the CSO outfall came as a surprise. However, there is mounting evidence that along the fringes of the harbor and in enclosed channels, sedimentation can be very rapid (Gallagher, Wallace & Eganhouse, 1992; Stolzenbach et al., 1993). This occurs because of weak tidal currents and the protected nature of small embayments especially in the southern portion of the harbor where subtidal flats are widespread. With cessation of sludge discharge to the harbor in 1991 and plans for reduction and improved treatment of CSO discharges, it is likely that the quality of the sediments near Fox Point will improve over time. However, because flushing is limited, recovery will probably be slow. This will be exacerbated by the activities of benthic organisms which tend to cause mixing of recently deposited (and presumably cleaner) particles with heavily contaminated sediments laid down in earlier times.

#### Acknowledgements

We appreciate the technical assistance of C.S. Phinney who performed GC/MS analyses and helped with data collection. We also wish to thank R.J. Pruell and M.H. Bothner and three anonymous reviewers who reviewed this paper and provided valuable comments. This work was supported by the Department of Environmental Protection, Office of Research and Standards, Commonwealth of Massachusetts.

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